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APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A  
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**FILING DATE: April 02, 2003**

**RELATED PCT APPLICATION NUMBER: PCT/US04/10330**

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# PROVISIONAL APPLICATION COVER SHEET

1132 U.S. PTO  
 04/02/03

This is a request for filing a PROVISIONAL APPLICATION under 35 CFR 1.53 (c).

Docket Number		62657	Type a plus sign (+) inside this box	+
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<b>**<input checked="" type="checkbox"/> Additional inventors are being named on separately numbered sheets attached hereto**</b>				
<b>TITLE OF THE INVENTION (280 characters max)</b>				
ORGANOSILICATE RESIN FORMULATION FOR USE IN MICROELECTRONIC DEVICES				
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<b>ENCLOSED APPLICATION PARTS (check all that apply)</b>				
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<input type="checkbox"/> A check or money order is enclosed to cover the Provisional filing fees			PROVISIONAL FILING FEE AMOUNT	
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government				
<input checked="" type="checkbox"/> No				
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are:				

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# PROVISIONAL APPLICATION COVER SHEET

Page 2

			Docket Number	62657
<b>TITLE OF THE INVENTION (280 characters max)</b>				
ORGANOSILICATE RESIN FORMULATION FOR USE IN MICROELECTRONIC DEVICES				
<b>INVENTOR(s)/APPLICANT(s) - Continued</b>				
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PROVISIONAL APPLICATION FILING ONLY

## ORGANOSILICATE RESIN FORMULATION FOR USE IN MICROELECTRONIC DEVICES

### BACKGROUND OF THE INVENTION

This invention relates to the use of organosilicate resins as hardmasks, etchstops or adhesion promotion layers in the fabrication of microelectronic devices, to a method of fabricating such devices, and to the resulting electronic devices.

The microelectronics fabrication industry is moving toward smaller geometries in its devices to enable lower power consumption and faster device speeds. As the conductor lines become finer and more closely packed, the requirements of the dielectrics between such conductors become more stringent. New materials having a lower dielectric constant than the dielectric constant for silicon dioxide, the traditionally used dielectric material, are being investigated. Among the dielectric materials that are attaining increased acceptance are spin-on, organic polymers having a dielectric constant of less than about 3.0. Polyarylenes, including polyarylene ethers and SiLK™ semiconductor dielectrics (from The Dow Chemical Company), are the primary organic polymeric dielectrics being considered.

The fabrication of microelectronic devices using these new dielectric materials has been reviewed, for example, in "Material Research Society (MRS) Bulletin, Oct 1997, Volume 22, Number 10". To date, however, the polyarylene dielectrics generally have been patterned in the traditional manner using inorganic hardmasks in forming patterns in the dielectric materials. Typically, the polyarylene dielectric is applied to the substrate and cured, followed by vapor deposition of an inorganic hardmask. A pattern is formed in the inorganic hardmask according to standard patterning practices, for example, application of a photoresist or softmask, followed by exposure and development of the softmask, pattern transfer from the softmask into the hardmask, and removal of the softmask. Etching of the hardmask is typically done using fluorine generating compounds. The underlying polyarylene dielectric can then be patterned. Deposition conditions must be carefully monitored to assure adequate adhesion between the hardmask and the polyarylene films.

Additional publications that discuss various methods and embodiments of dielectric materials, etch stops and hardmasks in fabrication of microelectronic devices include WO01/18861, which states that layers used as adjacent etchstop and dielectric materials should have substantially different etch selectivities. The publication also teaches that an inorganic layer (defined as one containing no carbon atoms) should be used as a via level and

metal level intermetal dielectric, and an organic, low dielectric constant, material should be used between the inorganic layers as an etch stop material.

WO00/75979 teaches a structure having a first dielectric layer which is an organic polymer and a second dielectric layer over the first layer which is a organohydridosiloxane. U.S. Patent 6,218,078 teaches the use of a spin on hardmask composition (a hydrogensilsesquioxane) which is coated over a low dielectric constant polymer (benzocyclobutene). U.S. Patent 6,218,317 teaches use of methylated oxide hardmasks over polymeric interlayer dielectric (ILD) materials. Advantageously, both hardmask and ILD formulations can be applied by spin-coating techniques.

Organosilicate resins include fully hydrolyzed or partially hydrolyzed reaction products of substituted alkoxy silanes or substituted acyloxy silanes, as disclosed for example in U.S. Patent 5,994,489 and WO 00/11096. WO 02/16477 teaches an organosilicate composition that is usefully employed as a hardmask in the fabrication of electronic devices. More particularly this composition comprises:

- (a) an alkoxy or acyloxy silane having at least one group containing ethylenic unsaturation which group is bonded to the silicon atom,
- (b) an alkoxy or acyloxy silane having at least one group containing an aromatic ring which group is bonded to the silicon atom, and
- (c) optionally an alkoxy or acyloxy silane having at least one group which is a C<sub>1</sub>-C<sub>6</sub> alkyl, which is bonded to the silicon atom. An acid catalyst, such as hydrochloric acid could be included to enhance cure properties.

#### SUMMARY OF THE INVENTION

According to the present invention there is provided an improved organosilicate composition usefully employed in the formation of a hardmask, etchstop or adhesion layer in the fabrication of electronic devices comprising:

- (a) an alkoxy or acyloxy silane having at least one group containing ethylenic unsaturation which group is bonded to the silicon atom
- (b) an alkoxy or acyloxy silane having at least one group containing an aromatic ring which group is bonded to the silicon atom,
- (c) a latent acid catalyst, and
- (d) optionally an alkoxy or acyloxy silane having at least one group which is a C<sub>1</sub>-C<sub>6</sub> alkyl, which is bonded to the silicon atom.

The foregoing composition is particularly effective when used in the process disclosed in the foregoing WO 02/16477 to form hardmasks, buried etchstops, or adhesion promoting layers in microelectronic devices. Due to the latent acid catalyst, the composition may be applied under conditions that would previously lead to premature curing. Moreover, the compositions are readily cured at reduced curing temperatures compared to formulations lacking in an acid catalyst.

Additionally, by utilizing photoactivated acid generating catalyst a selective hardmask composition that may be patterned and selectively etched is provided. According to this embodiment of the invention there is provided a method comprising:

- providing a substrate,
- forming a first layer on the substrate, wherein the first layer has a dielectric constant of less than 3.0 and comprises an organic polymer,
- applying an organosilicate resin comprising a photoactivated acid catalyst over the first layer,
- selectively exposing the organosilicate resin layer to a light pattern,
- removing the unexposed portion of the organosilicate resin to expose a portion of the first layer, and
- optionally, removing the exposed portions of the first layer.

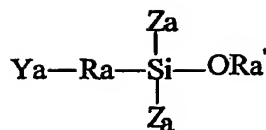
According to a second embodiment of the invention, a second layer of a low dielectric constant organic polymer is applied over the organosilicate layer. In this configuration, the organosilicate functions as a buried etch stop to control precisely the depth of trench in a dual damascene integration scheme. The buried etch stop may include a photoactivated catalyst and be patterned by photolithography where vias will penetrate into the first organic polymer dielectric layer. The etching of the buried etchstop layer may occur before or after coating of the second organic polymer layer depending upon what type of integration scheme is selected.

The invention is also an integrated circuit article comprising an active substrate containing transistors and an electrical interconnect structure containing a pattern of metal lines separated, at least partially, by layers or regions having a dielectric constant of less than 3.0 and comprising an organic polymer, wherein the article further comprises a layer of an organosilicate resin according to the invention above at least one layer of the organic polymer material.

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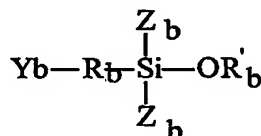
The term "alkylidene" refers to a divalent aliphatic hydrocarbon radical wherein both attachments to the remainder of the molecule are on the same carbon. The term "alkylene" refers to divalent radicals corresponding to the formula  $-(C_nH_{2n})-$ , wherein attachments to the remainder of the molecule are on different carbons. The term "aryl" refers to an aromatic radical, "aromatic" being defined as containing  $(4n+2)$  electrons, where  $n$  is an integer, as described in Morrison and Boyd, Organic Chemistry, 3rd Ed., 1973. The term "arylene" refers to a divalent aromatic radical. "Acyl" refers to a group having  $-C(O)R$  structure (e.g., a  $C_2$  acyl would be  $-C(O)CH_3$ ). "Acyloxy" refers to groups having  $-OC(O)R$  structure.

Preferred alkoxy or acyloxy silanes having at least one group containing ethylenic unsaturation for use herein correspond to the formula:



wherein Ra is C<sub>1</sub>-C<sub>6</sub> alkylidene, C<sub>1</sub>-C<sub>6</sub> alkylene, arylene, or a direct bond; Ya is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, a C<sub>2-6</sub> alkynyl, a C<sub>6</sub>-C<sub>20</sub> aryl, 3-methacryloxy, 3-acryloxy, 3-aminoethyl-amino, 3-amino, -SiZ<sub>2</sub>ORa', or -ORa'; Ra' is independently, in each occurrence, a C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>2</sub>-C<sub>6</sub> acyl ; and Za is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6-20</sub> aryl, or -ORa', with the proviso, that at least one of Ya, Za or Ra' is ethylenically unsaturated.

Preferred alkoxy or acyloxy silanes having at least one aromatic group for use herein correspond to the formula:

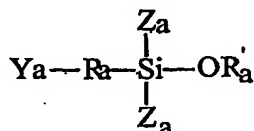


wherein Rb is C<sub>1</sub>-C<sub>6</sub> alkylidene, C<sub>1</sub>-C<sub>6</sub> alkylene, arylene, or a direct bond; Yb is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6</sub>-C<sub>20</sub> aryl, 3-methacryloxy, 3-acryloxy, 3-aminoethyl-amino, 3-amino, -SiZ<sub>b</sub>2ORb', or -ORb'; Rb' is independently, in each occurrence, a C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>2</sub>-C<sub>6</sub> acyl ; and Zb is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6-20</sub> aryl, or -ORb', provided at least one of Yb, Zb or Rb comprises an aromatic ring.

The silanes may be alkoxy silane, acyloxy silane, trialkoxy-silanes, triacetoxysilanes, dialkoxysilanes, diacetoxysilanes, tetraalkyoxysilanes or tetra-acetoxysilanes. Examples of some of the organic groups directly attached to the silicon atom include phenyl, methyl, ethyl, ethacryloxypropyl, aminopropyl, 3-aminoethylaminopropyl, vinyl, benzyl, bicycloheptenyl, cyclohexenylethyl, cyclohexyl, cyclopentadienyl, 7-octa-1-enyl, phenethyl, allyl and acetoxy.

Particularly preferred is a hydrolzyed or partially hydrolyzed product of a mixture comprising

(a) 50-95 mole percent silanes of the formula

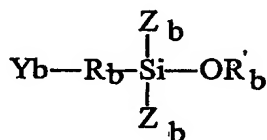


wherein Ra is C<sub>1</sub>-C<sub>6</sub> alkylidene, C<sub>1</sub>-C<sub>6</sub> alkylene, arylene, or a direct bond; Ya is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6</sub>-C<sub>20</sub> aryl, 3-methacryloxy, 3-acryloxy, 3-aminoethyl-amino, 3-amino, -SiZa<sub>2</sub>ORa', or -ORa'; Ra' is independently, in each occurrence, a C<sub>1</sub>-C<sub>6</sub>



alkyl or C<sub>2</sub>-C<sub>6</sub> acyl ; and Za is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6-20</sub> aryl, or -ORa', with the proviso, that at least one of Ya, Za or Ra' is ethylenically unsaturated,

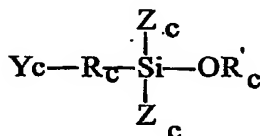
(b) 5 to 40 mole percent



wherein Rb is C<sub>1</sub>-C<sub>6</sub> alkylidene, C<sub>1</sub>-C<sub>6</sub> alkylene, arylene, or a direct bond; Yb is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6</sub>-C<sub>20</sub> aryl, 3-methacryloxy, 3-acryloxy, 3-aminoethyl-amino, 3-amino, -SiZb<sub>2</sub>ORb', or -ORb'; Rb' is independently, in each occurrence, a C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>2</sub>-C<sub>6</sub> acyl ; and Zb is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6-20</sub> aryl, or -ORb', provided at least one of Yb, Zb or Rb comprises an aromatic ring,

(c) a latent acid catalyst; and

(d) 0 to 45 mole percent



wherein Rc is C<sub>1</sub>-C<sub>6</sub> alkylidene, C<sub>1</sub>-C<sub>6</sub> alkylene, arylene, or a direct bond; Yc is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6</sub>-C<sub>20</sub> aryl, 3-methacryloxy, 3-acryloxy, 3-aminoethyl-amino, 3-amino, -SiZc<sub>2</sub>ORc', or -ORc'; Rc' is independently, in each occurrence, a C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>2</sub>-C<sub>6</sub> acyl ; and Zc is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6-20</sub> aryl, or -ORc', provided at least one of Zc or the combination of Rc-Yc comprises a C<sub>1-6</sub> alkyl group,

said mole percent is based on total moles of silanes (a), (b) and (d) present.

The manufacture of the hydrolyzed organosilane composition can be adjusted to give the properties desired, such as control of molecular weight, polymer architecture (for example, block copolymers, random copolymers, etc.) When combinations of organosilanes are used and one of the organosilanes is significantly more reactive than the other, it is preferable to continuously add the more reactive species during the hydrolysis reaction. This ensures that the residuals of both types of silanes are more uniformly distributed throughout the resulting oligomer or polymer. The rate of addition is adjusted to provide the desired mixture of residuals of the silanes in the resulting polymer. As used herein, "continuously add" means that the charge of the reactive silane is not added all at once but is rather added in at least several uniform portions or, more preferably is added uniformly throughout the

reaction.

Suitable latent acid catalysts are substances that generate an acid upon exposure to heat or light. Such compositions are herein referred to as thermal- acid generators (TAGs) or photo acid generators (PAGs). A mixture of two or more catalysts of one type, such as a mixture of two or more thermal acid generators, or a mixture of catalysts of different types, such as a thermal acid generator and photoacid generator, may be used advantageously in the present invention.

The amount of catalyst used is any amount that catalyzes the reaction, typically an amount from 0.1 to 25 percent by weight, based on the weight of the silane monomers in the composition. It is preferred that the catalyst is present in an amount in the range of 0.5 to 15 percent by weight, and more preferably in the range of 1 to 12 percent by weight.

The thermal acid generators useful in the present invention are any compounds which liberate acid upon heating, typically at a temperature in the range of about 25 to 220 °C. Suitable thermal acid generators useful in the present invention include, but are not limited to: 2,4,4,6- tetrabromocyclohexadienone, organic sulfonic acids, such as dinonylnaphthalene disulfonic acid, dinonylnaphthalene sulfonic acid, dodecylbenzene sulfonic acid and p-toluene sulfonic acid, alkyl esters of organic sulfonic acids, such as benzoin tosylate, and 2-nitrobenzyl tosylate, benzylic halogenated aromatic compounds, mono- and di-alkyl acid phosphates, mono- and di-phenyl acid phosphates, alkylphenyl acid phosphates, and combinations thereof. Blocked thermal acid generators, that is, acid esters, are preferred, such as blocked dodecyl sulfonic acid esters and blocked phosphonic acid esters. Such thermal acid generators are well known in the art and are generally commercially available, such as N ACURE brand blocked acid generators available from King Industries, Norwalk, Connecticut.

The photoacid generators useful in the present invention are any compounds which liberate acid upon exposure to light, typically at a wavelength of about 320 to 420 nanometers, however other wavelengths may be suitable as well. Suitable photoacid generators include halogenated triazines, onium salts, and sulfonated esters.

Particularly useful halogenated triazines include halomethyl-s- triazines. Suitable halogenated triazines include for example, 2-[1-(3,4- benzodioxolyl)]-4,6-bis(trichloromethyl)-1,2,5-triazine, 2-[1-(2,3- benzodioxolyl)]-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-[1-(3,4- benzodioxolyl)]-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-[1-(2,3- benzodioxolyl)]-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-(2- furfylethylidene)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-[2-(5- methylfuryl)ethylidene]-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-[2-(4- methylfuryl)ethylidene]-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-[2-(3- methylfuryl)ethylidene]-4,6-bis-(trichloromethyl)-1,3,5-triazine, 2-[2-(4, 5-

dimethylfuryl)ethylidene]-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-[2- (5-methoxyfuryl)ethylidene]-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-[2- (4-methoxyfuryl)ethylidene]-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-[2- (3-methoxyfuryl)ethylidene]-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-[2- (4,5-dimethoxyfuryl)ethylidene]-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-(2-(2-furfylethylidene)-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-[2-(5-methylfuryl)ethylidene]-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-[2-(4-methylfuryl)-ethylidene]-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-[2-(3-methylfuryl)ethylidene]-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-[2-(4,5-dimethoxyfuryl)ethylidene]-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-[2- (5-methoxyfuryl)ethylidene]-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-[2- (4-methoxyfuryl)ethylidene]-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-[2- (3-methoxyfuryl)ethylidene]-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-[2- (4,5-dimethoxyfuryl)ethylidene]-4,6-bis(tribromomethyl)-1,3,5-triazine, 2, 4,6-tris-(trichloromethyl)-1,3,5-triazine, 2,4,6-tris-(tribromomethyl)-1, 3,5-triazine, 2-phenyl-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-phenyl- 4,6-bis(tribromomethyl)-1,3,5-triazine, 2-(4-methoxyphenyl)-4,6- bis(trichloromethyl)-1,3,5-triazine, 2-(4-methoxyphenyl)-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-(2-(1-naphthyl)-4,6- bis(trichloromethyl)-1,3, 5-triazine, 2-(1-naphthyl)-4,6- bis(tribromomethyl)-1,3,5-triazine, 2-(4-methoxy-1-naphthyl)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-(4-methoxy-1-naphthyl)-4,6- bis(tribromomethyl)-1,3,5-triazine, 2-(4-chlorophenyl)-4,6- bis(tribromomethyl)-1,3,5-triazine, 2-styryl-4,6-bis(trichloromethyl)-1,3, 5-triazine, 2-styryl-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-(4- methoxystyryl)-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-(4- methoxystyryl)-4,6-bis(tribromomethyl)-1,3,5-triazine, 2-(3,4,5- trimethoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2(3,4,5- trimethoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-(3-chloro-1-phenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-(3-chlorophenyl)-4,6- bis(tribromomethyl)-1,3,5-triazine, and the like. Other triazine type photoacid generators useful in the present invention are disclosed in U.S. Pat. No. 5,366,846.

The s-triazine compounds are condensation reaction products of certain methyl-halomethyl-s-triazines and certain aldehydes or aldehyde derivatives. Such s-triazine compounds may be prepared according to the procedures disclosed in U.S. Pat. No. 3,954,475 and Wakabayashi et al., Bulletin of the Chemical Society of Japan, 42, 2924-30 (1969).

Onium salts with weakly nucleophilic anions are particularly suitable for use as photoacid generators in the present invention. Examples of such anions are the halogen complex anions of divalent to heptavalent metals or non-metals, for example, antimony, tin, iron, bismuth, aluminum, gallium, indium, titanium, zirconium, scandium, chromium, hafnium, copper, boron, phosphorus and arsenic. Examples of suitable onium salts include,

but are not limited to: diaryl-diazonium salts and onium salts of metals or metalloids of groups 1, 2, 5, 12, 15 or 16 of the Periodic Table, for example, halonium salts, quaternary ammonium, phosphonium and arsonium salts, aromatic sulfonium salts and sulfoxonium salts or selenium salts. Examples of suitable onium salts are disclosed in U.S. Pat. Nos. 4,442,197; 4,603,101; and 4,624,912.

Examples of the last mentioned onium salts include iodonium salts, sulfonium salts (including tetrahydrothiophenium salts), phosphonium salts, diazonium salts, and pyridinium salts. Specific examples thereof include diphenyliodonium-trifluoromethanesulfonate, diphenyliodoniumnonafluoro-n-butanesulfonate, diphenyliodoniumpyrenesulfonate, diphenyliodonium n-dodecylbenzenesulfonate, diphenyliodoniumhexafluoroantimonate, bis(4-t-butylphenyl)iodonium-trifluoromethanesulfonate, bis(4-t-butylphenyl)iodoniumnonafluoro-n-butanesulfonate, bis(4-t-butylphenyl)iodonium n-dodecylbenzenesulfonate, bis(4-t-butylphenyl)-iodoniumhexafluoroantimonate, bis(4-t-butylphenyl)-iodonium-naphthalenesulfonate, triphenylsulfoniumtrifluoromethanesulfonate, triphenylsulfoniumnonafluoro-n-butanesulfonate, triphenylsulfoniumhexafluoro-antimonate, triphenylsulfonium-naphthalenesulfonate, triphenylsulfonium-10-camphorsulfonate, 4-hydroxyphenylphenyl-methylsulfonium p-toluenesulfonate, cyclohexyl-2-oxocyclohexyl-methylsulfoniumtrifluoromethane-sulfonate, dicyclohexyl-2-oxocyclohexylsulfoniumtrifluoromethanesulfonate, 2-oxocyclohexyldimethylsulfoniumtrifluoromethanesulfonate, 4-hydroxyphenyl-benzyl-methylsulfonium p-toluenesulfonate, 1-naphthyl-dimethylsulfoniumtrifluoromethanesulfonate, 1-naphthyl-diethylsulfoniumtrifluoromethanesulfonate, 4-cyano-1-naphthyl-dimethylsulfoniumtrifluoromethanesulfonate, 4-nitro-1-naphthyl-dimethylsulfoniumtrifluoromethanesulfonate, 4-methyl-1-naphthyl-dimethylsulfoniumtrifluoromethanesulfonate, 4-cyano-1-naphthyl-diethylsulfoniumtrifluoromethanesulfonate, 4-nitro-1-naphthyl-diethylsulfoniumtrifluoromethanesulfonate, 4-methyl-1-naphthyl-diethylsulfoniumtrifluoromethanesulfonate, 4-hydroxy-1-naphthyl-dimethylsulfoniumtrifluoromethanesulfonate, 4-hydroxy-1-naphthyl-tetrahydrothiophenium-trifluoromethanesulfonate, 4-methoxy-1-naphthyl-tetrahydrothiophenium-trifluoromethanesulfonate, 4-ethoxy-1-naphthyl-tetrahydrothiopheniumtrifluoromethanesulfonate, 4-n-butoxy-1-naphthyl-tetrahydrothiopheniumnonafluoro-n-butanesulfonate, 4-methoxy-methoxy-1-naphthyl-tetrahydrothiopheniumtrifluoromethanesulfonate, 4-ethoxymethoxy-1-naphthyl-tetrahydrothiophenium-trifluoromethanesulfonate, 4-(1'-methoxyethoxy)-1-naphthyl-tetrahydrothiopheniumtrifluoro-methanesulfon ate, 4-(2'-methoxyethoxy)-1-

naphthyltetrahydrothiopheniumtrifluoro-methanesulfonate, 4-methoxycarbonyloxy-1-naphthyltetrahydrothiopheniumtrifluoromethanesulfonate, 4-ethoxycarbonyloxy-1-naphthyltetrahydrothiopheniumtrifluoromethanesulfonate, 4-n-propoxycarbonyloxy-1-naphthyltetrahydrothiophenium-trifluoromethanesulfonate, 4-i-propoxycarbonyloxy-1-naphthyl-tetrahydrothiopheniumtrifluoromethanesulfonate, 4-n-butoxy-carbonyloxy-1-naphthyltetrahydrothiopheniumtrifluoromethanesulfonate, 4-t-butoxycarbonyloxy-1-naphthyltetrahydro-thiopheniumtrifluoromethanesulfonate, 4-(2'-tetrahydro-furanyloxy)-1-naphthyltetrahydrothiopheniumtrifluoromethane-sulfonate, 4-(2'-tetrahydropyranyloxy)-1-naphthyltetrahydrothiopheniumtrifluoro-methanesulfonate, 4-benzyloxy-1-naphthyl-tetrahydrothiopheniumtrifluoromethane-sulfonate, and 1-(1'-naphthylacetomethyl)tetrahydrothiopheniumtrifluoromethane-sulfonate.

The sulfonated esters useful as photoacid generators in the present invention include sulfonyloxy ketones. Suitable sulfonated esters include, but are not limited to: benzoin tosylate, t-butylphenyl alpha-(p-toluenesulfonyloxy)-acetate, and t-butyl alpha-(p-toluenesulfonyloxy)-acetate. Such sulfonated esters are disclosed in the Journal of Photopolymer Science and Technology, vol. 4, No. 3, 337-340 (1991).

Additional suitable photoacid generators include sulfonic acid derivatives such as for example, alkyl sulfonate esters, alkyl sulfonic acid imides, haloalkyl sulfonate esters, aryl sulfonate esters, and iminosulfonates. Preferred embodiments of sulfonic acid derivatives include benzoin tosylate, pyrogallol tris(trifluoromethanesulfonate), nitrobenzyl-9,10-diethoxyanthracene-2-sulfonate, trifluoromethanesulfonylbicyclo-[2.2.1]hept-5-ene-2,3-dicarbodiimide, N-hydroxysuccinimidetrifluoromethane-sulfonate, and 1,8-naphthalenedicarboxylic acid imide trifluoromethanesulfonate.

Especially preferred sulfonic acid derivative photo acid generators include diphenyliodoniumtri-fluoromethanesulfonate, bis(4-t-butylphenyl)iodonium-trifluoromethanesulfonate, bis(4-t-butylphenyl)iodoniumnonafluoro-n-butanesulfonate, triphenylsulfoniumtri-fluoromethanesulfonate, triphenylsulfoniumnonafluoro-n-butanesulfonate, cyclohexyl 2-oxocyclohexyl methylsulfoniumtrifluoromethanesulfonate, dicyclohexyl 2-oxocyclohexylsulfonium-trifluoromethanesulfonate, 2-oxocyclohexyldimethyl-sulfoniumtrifluoromethane-sulfonate, 4-hydroxy-1-naphthyldimethylsulfoniumtri-fluoromethanesulfonate, 4-hydroxy-1-naphthyltetrahydrothiopheniumtrifluoromethane-sulfonate, 1-(1-naphthylacetomethyl)-tetrahydrothiopheniumtrifluoromethanesulfonate, trifluoromethanesulfonylbicyclo[2.2.1]hept-

5-ene-2,3-dicarboximide, N-hydroxysuccinimidetrifluoromethanesulfonate, and 1,8-naphthalene dicarboxylic acid imide trifluoromethanesulfonate.

Additional suitable photoacid generators include, for example, haloalkyl group containing hydrocarbon compounds and haloalkyl group containing heterocyclic compounds including (trichloromethyl)-s-triazine derivatives such as phenylbis(trichloromethyl)-s-triazine, 4-methoxy-phenylbis(trichloromethyl)-s-triazine, and 1-naphthylbis(trichloromethyl)-s-triazine; 1,1-bis(4'-chlorophenyl)-2,2,2-trichloroethane, and the like.

Additional suitable photoacid generators include diazoketone compounds, for example, 1,3-diketo-2-diazo compounds, diazobenzoquinone compounds and diazonaphthoquinone compounds. Preferred embodiments of diazoketones include 1,2-naphthoquinonediazido-4-sulfonylchloride, 1,2-naphthoquinonediazido-5-sulfonylchloride; 1,2-naphthoquinone-diazido-4-sulfonic acid ester or 1,2-naphthoquinonediazido-5-sulfonic acid ester of 2,3,4,4'-tetrahydroxybenzophenone; and 1,2-naphthoquinonediazido-4-sulfonic acid ester or 1,2-naphthoquinonediazido-5-sulfonic acid ester of 1,1,1-tris-(4'-hydroxyphenyl)ethane.

Additional suitable photoacid generators include sulfone compounds, for example, beta.-ketosulfone, .beta.-sulfonyl-sulfone, .alpha.-diazo derivatives of those compounds, and the like. As preferred embodiments of sulfone compounds, 4-trisphenacylsulfone, mesitylphenacylsulfone, and bis(phenylsulfonyl)methane may be mentioned.

Examples of preferred PAGs include (trifluoromethylsulfonyloxy)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboximide ("MDT"), onium salts, aromatic diazonium salts, sulfonium salts, diaryliodonium salts and sulfonic acid esters of N-hydroxyamides or -imides, as disclosed in U.S. Pat. No. 4,731,605. Also, a PAG that produces a weaker acid such as dodecane sulfonate of N-hydroxy-naphthalimide ("DDSN") may be used as well.

The organosilicate composition of the invention is suitably applied as one layer of a multilayer composition, optionally formed with partial etching of one or more layers, as in a damascene or dual damascene process. Highly, the organosilicate composition is deposited as a hard mask or etchstop over a first layer of an insulating material, preferably a layer of an organic polymer having a low dielectric constant.

As used herein, "organic polymer" means a polymer, which has primarily carbon in its backbone of the polymer chain, but may also include heteroatoms, such as oxygen (for example, polyarylene ethers) or nitrogen (see, for example, polyimides as described in Thin Film Multichip Modules, pp. 104-122, International Society for Hybrid Microelectronics, 1992). The organic polymer may contain small amounts of Si in the backbone but are, more preferably, free or essentially free of Si in the backbone. The first layer may contain pores.

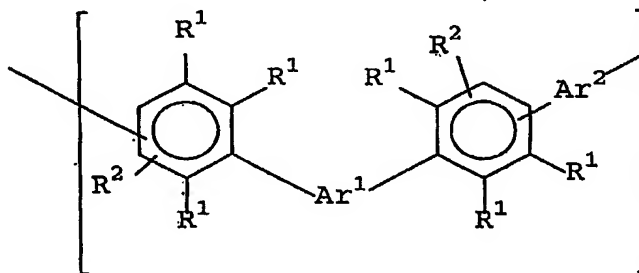
These pores may be helpful in further reducing the dielectric constant of the material. The layer may also contain adhesion promoters (including Si containing adhesion promoters), coating aids, and/or residual materials left after forming the pores. The amount of such additional components found in the first layer is preferably relatively small amounts, for example, less than 10 percent by weight, preferably less than 1 percent by weight, most preferably less than 0.1 percent by weight.

Preferably, the first layer is either a porous or non-porous polyarylene polymer. Examples of polyarylenes include the ring forming reaction product of aromatic cyclopentadienone and aromatic acetylene compounds as disclosed in U.S. Patent 5,965,679, poly(arylene ethers) as described in EP 0 755 957 B1, and other resins as disclosed in N. H. Hendricks and K.S.Y Liu, *Polym. Prepr.* (Am. Chem. Soc., Div. Polym. Chem.) 1996, 37(1), p. 150-1; also, J. S. Drage, et al., *Material Res. Soc., Symp. Proc.* (1997), Volume 476, (Low Dielectric Constant Materials III), pp. 121-128 and those described in U.S. Patent Nos. 5,115,082; 5,155,175; 5,179,188 and 5,874,516 and in PCT WO91/09081; WO97/01593 and EP 0755957-81). Additional suitable polymeric layers include cross-linked polyphenylenes, as disclosed in WO97/10193.

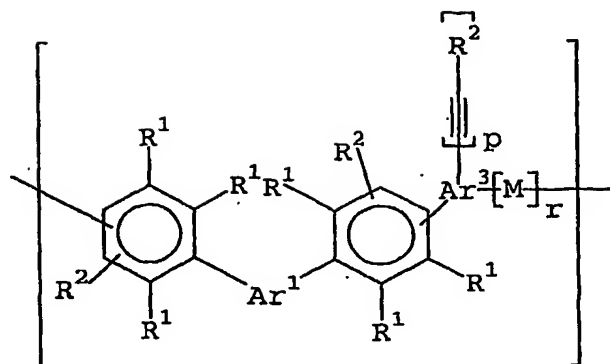
Most preferably, the first layer is a porous or non-porous polyarylene polymer which is the cured or cross-linked product of oligomers of the general formula:



wherein A has the structure:

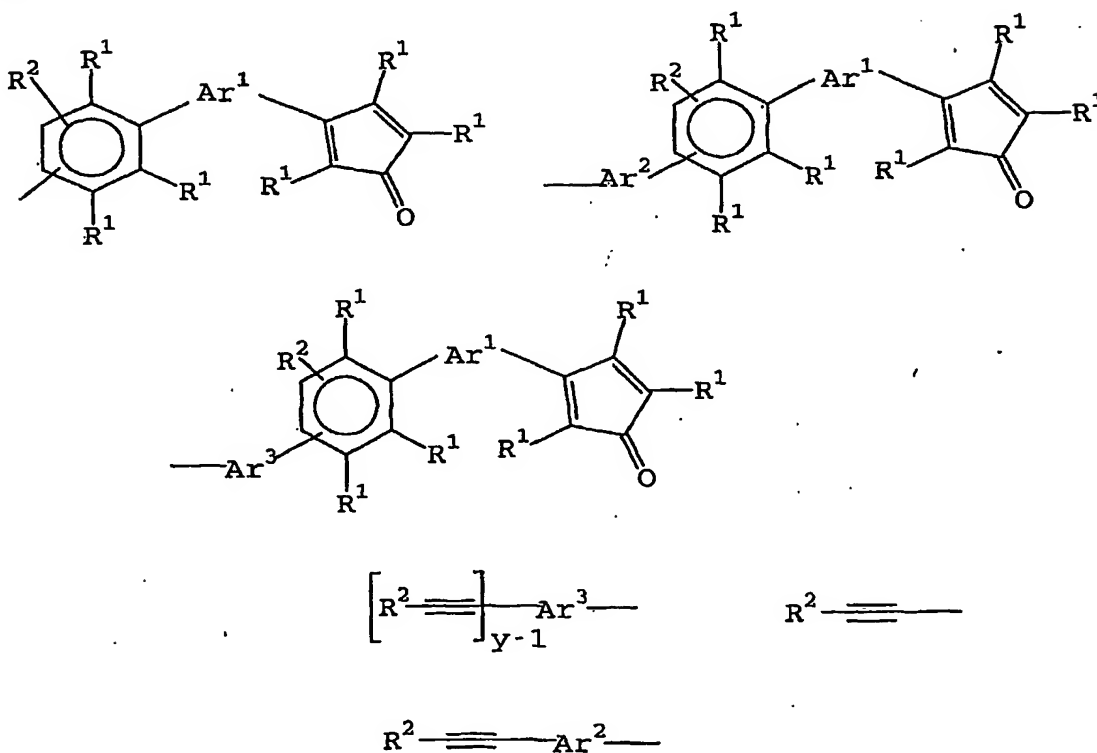


and B has the structure:



wherein EG are end groups having one or more of the structures:

EG=

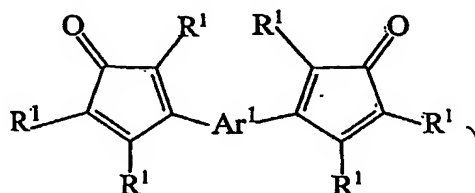


wherein  $R^1$  and  $R^2$  are independently H or an unsubstituted or inertly-substituted aromatic moiety and  $Ar^1$ ,  $Ar^2$  and  $Ar^3$  are independently an unsubstituted aromatic moiety or inertly-substituted aromatic moiety, M is a bond, and y is an integer of three or more, p is the number of unreacted acetylene groups in the given mer unit, r is one less than the number of reacted acetylene groups in the given mer unit and  $p+r=y-1$ , z is an integer from 1 to about 1000; w is an integer from 0 to about 1000 and v is an integer of two or more.



Such oligomers and polymers can be prepared by reacting a biscyclopentadienone, an aromatic acetylene containing three or more acetylene moieties and, optionally, a polyfunctional compound containing two aromatic acetylene moieties. Such a reaction may be represented by the reaction of compounds of the formulas

(a) a biscyclopentadienone of the formula:



(b) a polyfunctional acetylene of the formula:

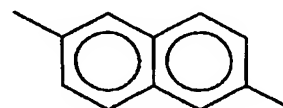
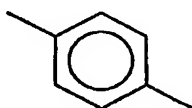
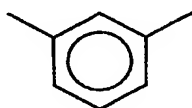


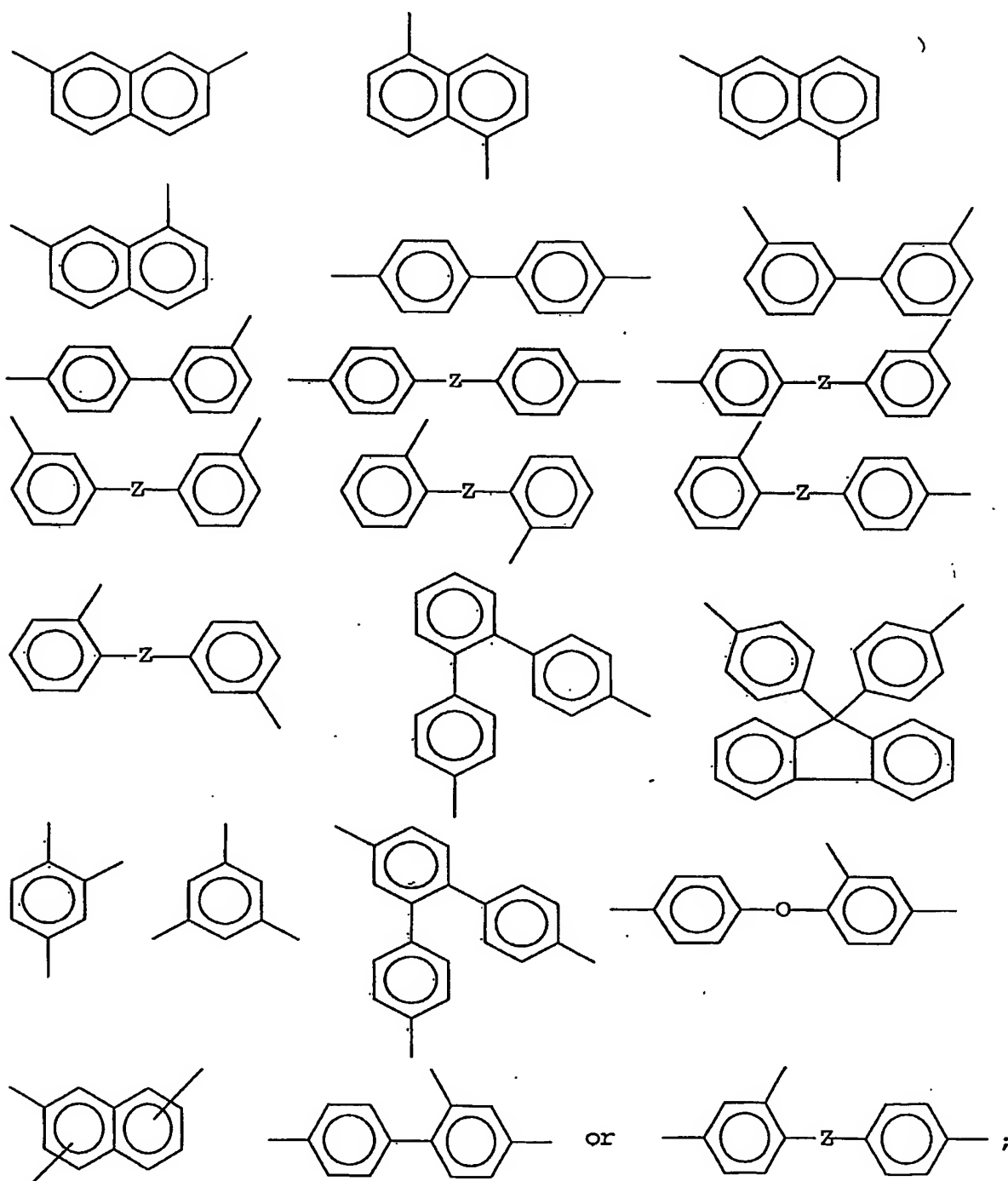
(c) and, optionally, a diacetylene of the formula:

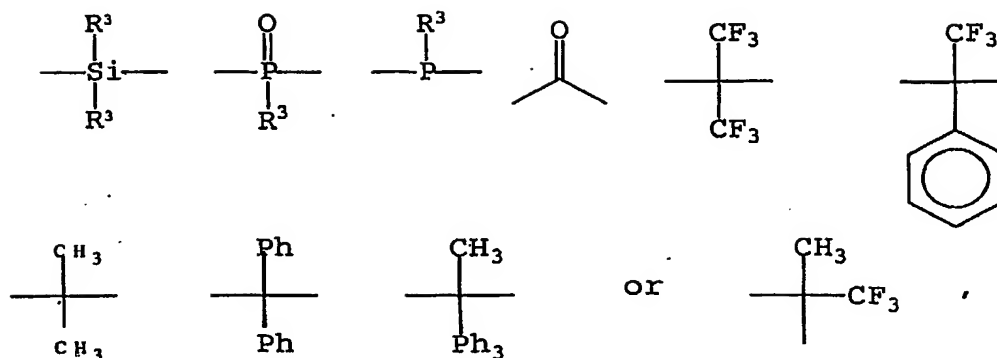


wherein  $R^1$ ,  $R^2$ ,  $\text{Ar}^1$ ,  $\text{Ar}^2$ ,  $\text{Ar}^3$  and  $y$  are as previously defined.

The definition of aromatic moiety includes phenyl, polyaromatic and fused aromatic moieties. "Inertly-substituted" means the substituent groups are essentially inert to the cyclopentadienone and acetylene polymerization reactions and do not readily react under the conditions of use of the cured polymer in microelectronic devices with environmental species, such as water. Such substituent groups include, for example, F, Cl, Br,  $-\text{CF}_3$ ,  $-\text{OCH}_3$ ,  $-\text{OCF}_3$ ,  $-\text{O-Ph}$  and alkyl of from one to eight carbon atoms, cycloalkyl of from three to about eight carbon atoms. For example, the moieties which can be unsubstituted or inertly-substituted aromatic moieties include:

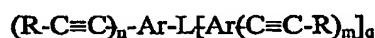




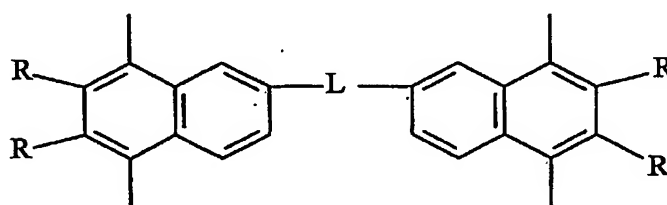


wherein each  $R^3$  is independently -H, -CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>3</sub>, -(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub> or Ph. Ph is phenyl.

A second preferred class of organic polymers are the reaction products of compounds of the formula:



wherein each Ar is an aromatic group or inertly-substituted aromatic group and each Ar comprises at least one aromatic ring; each R is independently hydrogen, an alkyl, aryl or inertly-substituted alkyl or aryl group; L is a covalent bond or a group which links one Ar to at least one other Ar; n and m are integers of at least 2; and q is an integer of at least 1, and wherein at least two of the ethynyl groups on at least one of the aromatic rings are *ortho* to one another. Preferably these polymers have the formula:



The substrate is preferably an electrically active substrate that includes, preferably, a semiconducting material, such as a silicon wafer, silicon-on-insulator, or gallium/arsenide. Preferably, the substrate includes transistors. The substrate may include earlier applied layers of metal interconnects and/or electrically insulating materials. These electrically insulating materials may be organic polymers as discussed above or could be other known dielectrics, such as silicon oxides, fluorinated silicon oxides, silicon nitrides, silsesquioxanes, etc. The earlier applied metal interconnects may have raised features, in which case the organic polymer or its precursor must be capable of filling the gaps between these features.

The organic polymeric dielectric is applied to the substrate by any known method that can achieve the desired thickness. Preferably, an uncured polymer or oligomer of the organic

polymer is spin coated from a solvent system at spin speeds of 500 to 5000 rpm. The thickness of the organic polymer layer is preferably less than 5000 nm, more preferably about 50 to about 2000 nm. Suitable solvents include mesitylene, pyridine, triethylamine, N-methylpyrrolidinone (NMP), methyl benzoate, ethyl benzoate, butyl benzoate, cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, cyclohexylpyrrolidinone, and ethers or hydroxy ethers, such as dibenzylethers, diglyme, triglyme, diethylene glycol ethyl ether, diethylene glycol methyl ether, dipropylene glycol methyl ether, dipropylene glycol dimethyl ether, propylene glycol phenyl ether, propylene glycol methyl ether, tripropylene glycol methyl ether, toluene, xylene, benzene, dipropylene glycol monomethyl ether acetate, dichlorobenzene, propylene carbonate, naphthalene, diphenyl ether, butyrolactone, dimethylacetamide, dimethylformamide and mixtures thereof.

The remaining liquid is then removed from the coating and the oligomer, or uncured polymer, is preferably cured by heating. Preferably, an initial heating step occurs on a hot plate under nitrogen at atmosphere, followed by a second high temperature cure on a hotplate or in a furnace. Cure temperatures for the preferred polyarylenes, disclosed in U.S. 5,965,679, are in the range of 50°C to 600°C, more preferably 100 to 450°C, for 0.1 to 60 minutes. In making porous first layers, special steps may need to be provided to burn out or otherwise remove a porogen. See, for example, WO 00/31183.

After applying (the application step may include a bake step to remove residual solvent) and, optionally, curing the first layer, the organosilicate material is applied. Any known coating process may be used, such as vapor deposition of monomers, spin coating, dip coating, spray coating, etc. However, spin coating of an oligomer or low molecular weight polymer solution is preferred. The thickness of the organosilicate layer is preferably greater than 50 Angstroms (5 nm), more preferably greater than 100 Angstroms. Preferably, the layer has a thickness of less than about 1000 Angstroms for a top hardmask and less than about 500 Angstroms for an embedded hardmask. According to a first embodiment, the organosilicate material is cured, preferably at temperatures of 50 to 500, more preferably 100 to 400°C for 0.1 to 60 minutes. The precise temperatures will depend on the organosilicate material selected.

A photoresist may be applied over the organosilicate material before curing, if desired. The photoresist is imaged and developed according to conventional methods to remove a portion of the photoresist exposing a pattern on the hardmask. The organosilicate hardmask may then be etched in turn to expose a portion of the first layer dielectric. Etching of the organosilicate hardmask may occur by a variety of methods, such as wet etch (for example, electrochemical, photoelectrochemical or open circuit etching) or dry etch (for example, vapor, plasma, laserbeam, e-beam, ion) techniques as described in Etching in

Microsystems, Michael Kohler, Wiley-VCH. The photoresist may be removed during etching or in a separate removal step. The exposed portion of the first dielectric layer may then be etched by such methods as wet or dry etching to form a trench, via or other desired feature. If desired, a second organic polymer layer may then be applied and cured over the patterned organosilicate layer. A second hardmask of any type, but preferably again an organosilicate, may be applied over the second organic polymer layer and patterned according to standard processes. The organic polymer can then be etched down to the embedded hardmask or etch stop and where a pattern has been opened in the embedded hardmask, down through the first layer of organic polymer.

According to another embodiment, after being applied over a first organic polymer dielectric layer, the organosilicate material is cured, preferably at temperatures of 50 to 500°C, more preferably 100 to 400°C for 0.1 to 60 minutes. The precise temperatures will depend on the organosilicate material selected. A second layer of the organic polymer dielectric is then be applied by any of the coating methods previously mentioned and a full or partial cure of the organic polymer layer completed. A variety of dual damascene processes can be used to construct both trench and via structures using the embedded organosilicate layer as an etch stop to control the uniformity, depth, and/or shape of the trenches. The organosilicate hardmask may then be etched to expose a portion of the first layer dielectric. Etching of the organosilicate hardmask may occur by variety of methods, such as wet etch (e.g., electrochemical, photoelectrochemical or open circuit etching) or dry etch (e.g., vapor, plasma, laserbeam, e-beam, ion) etch techniques as described in Etching in Microsystems, Michael Kohler, Wiley-VCH. The exposed portion of the first dielectric layer may then be etched by such methods as wet or dry etching to create a via or other desired feature.

Chemical mechanical polishing to enhance planarization and/or remove surface layers or features may also be used according to known methods. Cleaning steps to remove photoresists and other residual layers may also be used as is known.

Note that since the organosilicate hardmask itself has a low dielectric constant it may be convenient to use it as an embedded hardmask, which is not removed from the article, but rather has additional interconnect/dielectric layers applied over it. Alternatively, the organosilicate hardmask may be removed by any known process, for example, oxygen/solvent treatment, thermal degradation plus solvent cleaning, etc.

One important factor that enables the organosilicate resin to be used as a hardmask for the organic polymer dielectrics is that organosilicate resins are relatively resistant to the chemistries used to etch the organic polymer dielectrics. Etch selectivity can be defined as the thickness of the organic polymer dielectric divided by the thickness of organosilicate

removed when exposed to the same etch chemistry. According to this invention, preferably an etch selectivity of at least 3, more preferably at least 5, is present. For the hydrolyzed silanes, etch selectivity may be higher - on the order of greater than 10, preferably greater than 20. Etch selectivities can be increased by performing treatments, such as exposure to fluorinated plasmas, and irradiation with light or e-beams on the BCB based organosilicates.

Some of the benefits of the present invention become clearer when examined in the form of some specific examples.

One approach uses a non-sacrificial (that is, the layer is not removed but rather becomes a permanent part of the device), non-photodefinable organosilicate. This allows for the replacement of a vapor phase deposited hardmask with a low permittivity spin-on deposited hardmask. Standard patterning practices still apply. An improvement in performance in the device is obtained due to a decrease in the combined dielectric constant of the multilayered dielectric stack. The relative permittivity of the spin on hardmask of this invention is between 3.2, preferably 3.0, and 1.8 and compared to standard vapor phase hardmasks having a relative permittivity between 9 and 3.0. Secondly, a cost reduction is obtained due to the lower cost-of-ownership intrinsic to spin-on dielectrics.

A second approach uses a sacrificial (that is, the layer is removed), non-photodefinable organosilicate resin. Standard patterning practices still apply. After the patterning step, a dedicated processing step involving, for example, an oxygen and solvent treatment is used to remove the sacrificial spin-on hardmask. Due to the removal of this layer, the lowest possible dielectric constant is obtained. An increase in yield and reliability is obtained due to a decrease in number of interfaces in the multilevel build.

A third approach uses a non-sacrificial, photodefinable organosilicate. In addition to the benefits noted in the first approach, an increase in yield is anticipated due to the lowered probability of processing induced defects. Also, the need for photoresists and softmasks is reduced or eliminated.

A fourth approach uses a sacrificial, photodefinable organosilicate. The benefits noted in the second approach still apply with the added benefits of an increase in yield due to the lowered probability of processing-induced defects and simplification of the processing due to elimination of the need for the photoresists or softmasks.

Additional variations on the method of this invention are exemplified by the following examples which are provided for illustrative purposes only and are not intended to limit the scope of this invention. Unless stated to the contrary all parts and percentages are based on weight.

#### Example 1

##### A) Synthesis of 90/10 mole percent Vinyl/Phenyl Organosilicate

A 250 ml, 3 neck round bottom flask was placed in a 20°C water bath and fitted with a stirrer connected to an air motor, a water jacketed condenser, a thermocouple connected to a temperature controller, and an addition funnel. 21.6 Grams (1.2 moles) of acidified water (3N acetic acid) was added to the flask. 53.3 grams (0.3601 moles) of vinyltrimethoxysilane and 7.94 grams (0.0401 moles) of phenyltrimethoxysilane were pre-mixed and added to the addition funnel. The silanes were added to the reactor over 45 minutes. After the addition was complete the water bath was removed and a heating mantle was placed under the flask. The addition funnel was removed and a dean-stark trap and a nitrogen sweep line were attached. The solution was slowly heated to 100°C. While heating to 100°C methanol and acetic acid were collected in the trap. When the reaction reached 100 °C, 100 grams of propyleneglycol monomethylether acetate was added. The solution was slowly heated to 125°C while collecting additional methanol. When the temperature reached 125°C the trap was removed and the reaction held for 3 hours at 125°C. After 3 hours heating was discontinued and 75 grams of propyleneglycol monomethylether acetate was added and the solution was mixed until reaching room temperature. Aliquots were taken after the silane addition, at 100°C, at 125°C and every 30 minutes until the end of the process for molecular weight measurement, molecular weight distribution (PD) and solubility testing. Results are contained in Table 1.

Table 1 – MW Data

Sample	Mn	Mw	Mz	PD	Comments
1	457	481	510	1.05	At 100 °C
2	971	1400	2260	1.44	At 125 °C
3	1260	2380	4980	1.88	30 min @ 125 °C
4	1510	3390	7950	2.25	60 min @ 125 °C
5	1870	5580	15000	2.99	90 min @ 125 °C
6	2080	7560	23100	3.64	120 min @ 125 °C
7	2250	9680	30400	4.3	150 min @ 125 °C
8	2270	13700	50800	6.02	180 min @ 125 °C

##### B) UV Curable Formulation Preparation, Cure and Solubility Testing

Organosilicate solutions 1, and 4-8 from Table 1 were diluted uniformly to 15 percent solids content in propyleneglycol monomethyl ether acetate and spincoated using a Chemat

Technology KW-4A spin coater to four inch (10 cm) silicon wafers. The solutions were spun for 18 seconds at 300-420 rpm followed by 30 seconds at 500-680 rpm. To eliminate the solvent, the wafers were placed in an oven at 130°C for one minute. When the wafer was cool a portion was immersed in the developer solution (MF-CD-26 Mucroposit Developer, available from Shipley Chemical Company) for 30 seconds. After immersion the wafer was rinsed with deionized water and blown dry with air. Solutions 7 and 8 were insoluble in the developer after 30 second immersion. Solution 8 was still insoluble after 120 second immersion whereas, solution 7 was only marginally soluble (some coating remained). Solutions 5 and 6 were marginally soluble after 30 second immersion with only slightly more film dissolving after 120 second immersion (some coating still visible on the wafer). Solutions 1 and 4 were completely soluble in developer after 30 second immersion.

To 6 g of solution 4, 0.072 g of a photo acid generating catalyst (mixed triarylsulfonium hexafluoroantimonate salts, CYRACURE® UVI-6976 available from The Dow Chemical Company) was added and mixed until homogenous. A four inch (10 cm) silicon wafer was spincoated using the process described above. The wafer was placed in an oven at 130°C for one minute. When the wafer was cool it was exposed to UV radiation (H bulb) in air at 10 ft/min (3M/min) with a 4" (10 cm) part to bulb height. The wafer was immersed in the developer solution for 30 and then 120 seconds. The coating was insoluble in the developer after both 30 second and 120 second immersion, demonstrating that the coating was converted to a photocurable hardmask upon exposure to the UV light.

## Example 2

Photo hard mask compositions for imaging were prepared by adding 8 percent (based on resin solids) of a cationic photoacid generator (mixed triarylsulfonium hexafluoroantimonate salts, CYRACURE® UVI-6976 available from The Dow Chemical Company) to representative organosilicate resins (100 percent vinyltrimethoxysilane or a mixture (95:5 mole:mole) of vinyltrimethoxysilane and phenyltrimethoxysilane). Compositions were diluted to ~15 percent solids using propylene glycol methyl ether acetate solvent (Dowanol™ PMA from The Dow Chemical Company) and then filtered through 0.22 micron PTFE filters. Approximately 2 ml of the photo hard mask composition was dispensed (puddled) onto a static 4 inch (10 cm) silicon wafer. After dispensing, the wafer was initially spun at 500 RPM for 5 seconds, followed by a second spin cycle at 2000 or 5000 RPM for 30 seconds using a spin coater (Model 5100, Solitec Inc.). After applying the photo hard mask composition, the coated silicon wafer was pre-exposure baked on a direct hotplate (Model VBS-200, Solitec Inc.) at 150°C for 60 seconds.



Light exposure and imaging were carried out using 365 nm (I-line) ultraviolet light from a Karl Suss Mask Aligner (Model MA 150). The dosage was varied from 5 to 250 mJ/cm<sup>2</sup> using a multi-transmission quartz mask, which consisted of vias between 3 and 100 microns. After light exposure, the coated silicon wafer was post-baked on a direct hotplate (Model VBS-200, Solitec Inc.) at 220°C for 60 seconds. Development was performed by immersing coated wafers in 2.38 percent aqueous tetramethylammonium hydroxide (TMAH) solution and then rinsing with deionized water. As a final step, the developed wafers were placed in a spin, rinse, dryer tool (PSC-102, Semitool) at 2000 RPM for 600 seconds to afford the negative image. Results are contained in Table 2

Table 2

Composition	Mw	Development Time in TMAH (sec.)	Smallest Via that Completely Opened (μm)
100	7000	180	25
95:5	2000	10	15
"	"	30	15

### Example 3

90:10 Vinyl:Phenyl Organosilicate Resin (MW = 2120).

The reaction conditions of Example 2 were substantially repeated using a 90:10 mole:mole mixture of vinyltrimethoxysilane and phenyltrimethoxysilane. Samples included 8 percent CYRACURE® UVI-6976 and were spun at 500 RPM for 5 seconds, followed by a second spin cycle at 5000 RPM for 30 seconds, and then pre-exposure baked at 55°C for 60 seconds. After exposure, films were post-baked at 180°C for 60 seconds. Films were developed in 2.38 percent aqueous TMAH. Results are contained in Table 3.

Table 3

<u>Radiation</u> <u>Dosage (mJ/cm<sup>2</sup>)</u>	<u>Smallest Via that</u> <u>completely opened (μm)</u>
50.0	35
45.6	25
30.9	25
14.7	15
6.7	15

Claims:

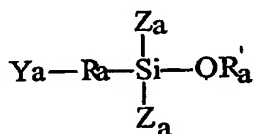
1. An organosilicate composition that is usefully employed in the formation of a hardmask, etchstop or adhesion promoting layer in the fabrication of electronic devices comprising:

- (a) an alkoxy or acyloxy silane having at least one group containing ethylenic unsaturation which group is bonded to the silicon atom
- (b) an alkoxy or acyloxy silane having at least one group containing an aromatic ring which group is bonded to the silicon atom,
- (c) a latent acid catalyst, and
- (d) optionally an alkoxy or acyloxy silane having at least one group which is a C<sub>1</sub>-C<sub>6</sub> alkyl, which is bonded to the silicon atom.

2. The composition of claim 1 wherein the first silane (a) is a vinyl acetoxy silane and the second silane (b) is an arylalkoxysilane.

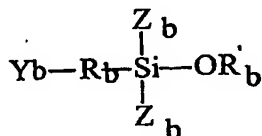
3. The composition of claim 1 wherein the combination comprises

(a) 50-95 mole percent silanes of the formula



wherein R<sub>a</sub> is C<sub>1</sub>-C<sub>6</sub> alkylidene, C<sub>1</sub>-C<sub>6</sub> alkylene, arylene, or a direct bond; Y<sub>a</sub> is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6</sub>-C<sub>20</sub> aryl, 3-methacryloxy, 3-acryloxy, 3-aminoethyl-amino, 3-amino, -SiZ<sub>a</sub>2OR<sub>a</sub>', or -OR<sub>a</sub>'; R<sub>a</sub>' is independently, in each occurrence, a C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>2</sub>-C<sub>6</sub> acyl; and Z<sub>a</sub> is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6-20</sub> aryl, or -OR<sub>a</sub>', with the proviso, that at least one of Y<sub>a</sub>, Z<sub>a</sub> or R<sub>a</sub>' is ethylenically unsaturated,

(b) 5 to 40 mole percent

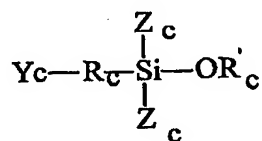


wherein R<sub>b</sub> is C<sub>1</sub>-C<sub>6</sub> alkylidene, C<sub>1</sub>-C<sub>6</sub> alkylene, arylene, or a direct bond; Y<sub>b</sub> is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6</sub>-C<sub>20</sub> aryl, 3-methacryloxy, 3-acryloxy, 3-aminoethyl-amino, 3-amino, -SiZ<sub>b</sub>2OR<sub>b</sub>', or -OR<sub>b</sub>'; R<sub>b</sub>' is independently, in each occurrence, a C<sub>1</sub>-C<sub>6</sub>

alkyl or C<sub>2</sub>-C<sub>6</sub> acyl ; and Zb is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6-20</sub> aryl, or -ORb', provided at least one of Yb, Zb or Rb comprises an aromatic ring,

(c) a latent acid catalyst; and

(d) 0 to 45 mole percent



wherein Rc is C<sub>1</sub>-C<sub>6</sub> alkylidene, C<sub>1</sub>-C<sub>6</sub> alkylene, arylene, or a direct bond; Yc is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6</sub>-C<sub>20</sub> aryl, 3-methacryloxy, 3-acryloxy, 3-aminoethyl-amino, 3-amino, -SiZc<sub>2</sub>ORc', or -ORc'; Rc' is independently, in each occurrence, a C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>2</sub>-C<sub>6</sub> acyl ; and Zc is C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkenyl, C<sub>2-6</sub> alkynyl, C<sub>6-20</sub> aryl, or -ORc', provided at least one of Zc or the combination of Rc-Yc comprises a C<sub>1-6</sub> alkyl group

4. The composition of claim 1 comprising both a photoacid generator and a thermal acid generator.

5. The hydrolyzed or partially hydrolyzed product of a combination of silanes according to any one of claims 1-4

6. A method comprising  
 providing a substrate,  
 forming a first layer on the substrate, wherein the first layer has a dielectric constant of less than 3.0 and comprises an organic polymer,  
 applying an organosilicate composition over the first layer, and  
 hydrolyzing the organosilicate composition to form an organosilicate resin,  
 characterized in that the organosilicate composition is a composition according to any one of claims 1-4.

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(a) an alkoxy or acyloxy silane having at least one group containing ethylenic unsaturation which group is bonded to the silicon atom

(c) a latent acid catalyst, and

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